Zn incorporation and band gap shrinkage in *p*-type GaAs

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Dimethylzinc (DMZn) was used as a *p*-type dopant in GaAs grown by low pressure metalorganic vapor phase epitaxy using trimethylgallium and arsine (AsH_3) as source materials. The hole carrier concentrations and zinc (Zn) incorporation efficiency are studied by using the Hall effect, electrochemical capacitance voltage profiler and photoluminescence (PL) spectroscopy. The influence of growth parameters such as DMZn mole fraction, growth temperature, and AsH_3 mole fraction on the Zn incorporation have been studied. The hole concentration increases with increasing DMZn and AsH_3 mole fraction and decreases with increasing growth temperature. This can be explained by vacancy control model. The PL experiments were carried out as a function of hole concentration ($10^{17}-1.5\times10^{20}$ cm^{-3}). The main peak shifted to lower energy and the full width at half maximum (FWHM) increases with increasing hole concentrations. We have obtained an empirical relation for FWHM of PL, $\Delta E(p)(\mathrm{eV})=1.15\times10^{-8}p^{1/3}$. We also obtained an empirical relation for the band gap shrinkage, ΔE_g in Zn doped GaAs as a function of hole concentration. The value of $\Delta E_g(\mathrm{eV})=-2.75\times10^{-8}p^{1/3}$, indicates a significant band gap shrinkage at high doping levels. These relations are considered to provide a useful tool to determine the hole concentration in Zn doped GaAs by low temperature PL measurement. The hole concentration increases with increasing AsH_3 mole fraction and the main peak is shifted to a lower energy side. This can be explained also by the vacancy control model. As the hole concentration is increased above 3.8 $\times10^{18}$ cm^{-3}, a shoulder peak separated from the main peak was observed in the PL spectra and disappears at higher concentrations.
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I. INTRODUCTION

Metalorganic vapor phase epitaxy (MOVPE)[1] is well known for the growth of multilayered structures of compound semiconductors and optoelectronic device fabrication.[2] Many applications require sharp interfaces and controlled doping of impurities in the semiconductors. In addition to high optical and electrical quality of the films, the heavily doped epitaxial film for optoelectronic device applications requires mirror smooth surface morphology, which is often difficult to obtain due to lattice dilation.[3,4] Therefore it is necessary to understand the influence of the growth parameters, which determine the layer quality.

The effect of *p*-type heavy doping ($>10^{19}$ cm^{-3}) in GaAs is an important issue of the optical and electrical properties not only from a fundamental understanding but also for the device applications, such as heterojunction bipolar transistors (HBTs)[5] and laser diode.[6] The heavy doping affects the density of states, band structure, carrier mobility, absorption, luminescence properties, and hence the device properties. For example the heavy doping is used either in the base or contact layer of the HBTs and the active layer of laser diodes. Also the high doping effects the band gap shrinkage and by a band tail extending into the gap. In HBTs, the heavy *p*-type doping affects the shrinkage of band gap[7–13] of the base, which enhances the emitter injection efficiency, thus affecting the performance of the Np^+n (N, n, and p^+ are electron and hole densities) HBTs.[5] Band gap shrinkage due to heavy doping is a well known phenomenon in III-V compound semiconductors, particularly observed in GaAs by photoluminescence (PL) spectroscopy.[8,13–20] In the heterojunction-based devices, the band gap shifts due to heavy doping result in valence and conduction band discontinuity of the heterojunction interface.[21]

The *p*-type doping in GaAs can be obtained by C, Be, Zn, or Mg as doping sources. Among these doping sources Zn is the most common dopant in GaAs and AlGaAs, although the diffusion coefficient of Zn in these III-V compound semiconductors is high.[22] Still it is preferred because Zn precursors can be handled very easily, and high doping efficiency ($10^{16}-10^{20}$ cm^{-3}), uniform doping can be obtained easily. Zn doping has always shown low memory effects, a relatively small amount of deep level traps,[23] and good surface morphology even at high doping levels. Because of the different electrical and optical properties of Zn doped GaAs from C-doped GaAs[7,8,11,17,24] grown by metalorganic vapor phase epitaxy (MOVPE), these properties have been studied extensively by several authors in recent years.[25–30] Moreover, the identification of luminescent prop-

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[a)] Electronic mail: sbk@mrc.iisc.ernet.in erties is still controversial in the heavily doped region.[31] The dominant peak in the PL spectrum, at low temperature due to band-to-band (B-B) or band-to-acceptor ($e-A$) transitions are also the subject of some controversy.[8,25] In addition, it has been suggested that the shoulder peak at the high energy side may be due to K-nonconserving (nonvertical transition),[8] which was counter argued by Sernelius's[32] result. This prompted us to conduct a systematic study of Zn doping in GaAs.

PL spectroscopy is the most common characterization technique for investigating the distribution of defects, concerning the type and heavy doping effect in GaAs, hence employed in our work. It is a nondestructive and noncontact technique for examining the band structure and luminescence properties of GaAs. The luminescence properties are dependent on the growth conditions (or methods), impurity species, doping concentrations, and growth temperatures. It has also been employed to investigate the Fermi level of heavily p-type doped materials,[9] the carrier concentration,[7] and the epitaxial layer quality.[10] The effects of growth parameters such as DMZn mole fraction, growth temperatures, and arsine (AsH_3) mole fraction on Zn incorporation in GaAs are investigated thoroughly and these results are compared with published literatures.[8,12,14–20,25,28] We are reporting the luminescence properties of Zn doped GaAs with the varying AsH_3 mole fraction for the first time. After thorough investigation of Zn doped GaAs, we have suggested a relationship of full width at half maximum (FWHM) versus hole concentration of Zn doped GaAs and band gap shrinkage, which could be considered a useful tool to determine the free hole concentration in Zn doped GaAs by low temperature PL measurement. The hole carrier concentration increases with increasing DMZn mole fraction and AsH_3 mole fraction and decreases with increasing growth temperature. A vacancy control model was found to be consistent with our results. We have observed the shoulder peak at a high energy side of Zn doped GaAs at the hole concentration above 3.8×10^{18} cm^{-3} and disappear at concentration greater than 8×10^{19} cm^{-3}.

II. EXPERIMENT

The Zn doped p-type GaAs as grown in a low pressure horizontal MOVPE reactor on both Cr doped semi-insulating and Si doped n^+-GaAs (100) substrates with an offset by 2° towards the [110] direction. The source materials were trimethylgallium (TMGa), arsine (AsH_3), and dimethylzinc (DMZn) as a p-type dopant and palladium purified H_2 as a carrier gas. During the growth the pressure inside the reactor was kept at 100 Torr and the growth temperature was varied from 550 °C to 725 °C. TMGa flow rate was kept constant at 10 sccm and the AsH_3 flow rate was varied from 30 to 50 sccm in order to obtain different V/III ratios. The total flow rate was about 2 slpm. The growth rate was varied between 470 and 800 Å/min. The details of the growth procedure can be found elsewhere.[33]

The doping concentrations were determined by using both Bio-Rad electrochemical capacitance-voltage (ECV) polaron profiler and Hall measurement. The Hall effect by the Van der Pauw method was carried out at 300 K for mobility measurement, considering the Hall factor $r_H = 1$. p-type layers with a thickness of about 1.2 μm were chosen for analysis to reduce thickness measurement errors. Hole densities in the range of $10^{17} - 1.5 \times 10^{20}$ cm^{-3} were measured.

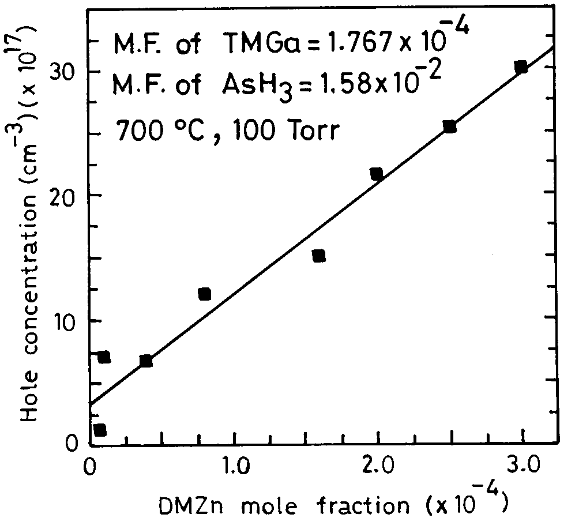

FIG. 1. Hole concentration of zinc doped GaAs as a function of DMZn mole fraction.

PL measurements were carried out using a MIDAC Fourier transform PL (FTPL) system at a temperature from 4.2 to 300 K. Argon ion laser operating at a wavelength of 5145 Å was used as a source of excitation. The exposed area was about 3 mm^2. The PL signal was detected by a LN_2 cooled Ge photodetector whose operating range is about 0.75–1.9 eV, while resolution was kept at about 0.5 meV.

III. RESULTS AND DISCUSSION

A. Electrical properties

1. Effect of variation of DMZn mole fraction and growth temperature

The surface of epilayers is influenced by the growth parameters, such as pressure inside the reactor tube, growth temperature, substrate orientation, AsH_3/TMGa mole ratio, etc. The surface of Zn doped p-type GaAs appears to be mirror smooth over a wide range of temperature (600–725 °C) in this study. Figure 1 shows the hole concentration as a function of DMZn mole fraction.

The hole concentration increases linearly with DMZn mole function, which is consistent with that described by Glew.[34] The hole concentration is observed to increase as the growth temperature decreases as shown in Fig. 2 for a fixed DMZn mole fraction. The strong temperature dependence of Zn incorporation is believed to be a result of evaporation of Zn atoms from the growth surface due to increased vapor pressure at higher temperatures. The vapor pressure of Zn is inversely proportional to the Zn incorporation and is given by

$$P_{\mathrm{zn}} = P_0 \exp(-E_0/KT_G),$$

where P_0 is a pre-exponential factor, T_G is the growth temperature, and E_0 is the activation energy. Between 600 and

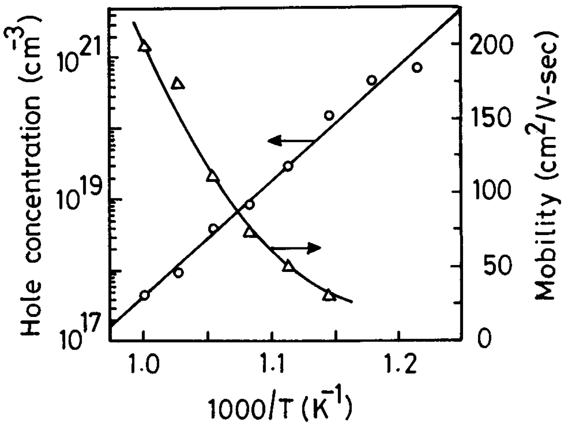

FIG. 2. 300 K hole carrier concentrations and hole mobilities for Zn doped GaAs epilayers grown under various growth temperatures.

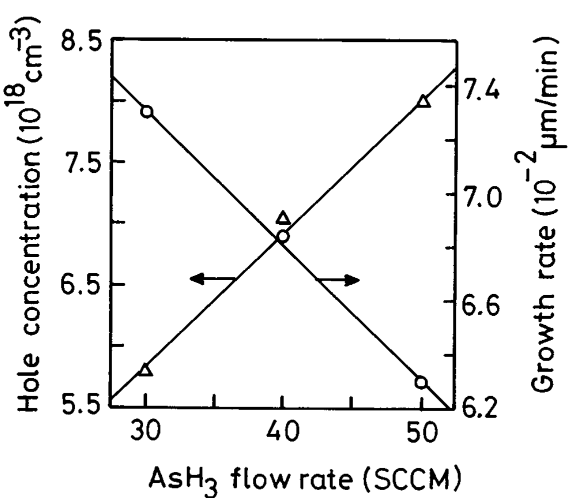

FIG. 3. Hole concentration and growth rate as a function of AsH$_3$ flow rate.

725 °C the incorporation activation energy of DMZn from the slope of the Arrhenius plot is around 3.2 eV, which is in agreement with the earlier reported results by Bass and Oliver[35] and Glew.[34] The surface morphology of Zn doped layers is polycrystalline in the range of temperature 550–575 °C. TMGa decomposes rapidly above 500 °C in a MOVPE reactor. Between 500 and 550 °C cracked AsH$_3$ concentration is normally low. This has been suggested due to the lack of cracked AsH$_3$ concentration on the growth surface.[2] Glew[34] suggested that Zn metalorganics can promote arsenic decomposition. TMGa is known to catalyze AsH$_3$ decomposition. Above 575 °C the concentration of arsenic is significant[2] and plays a major role in the growth kinetics. In a cracked furnace As$_2$ and As$_4$ concentrations reach a maximum at 675 °C, while in an MOVPE system the decomposition is complete by 700 °C. GaAs hole concentrations of Zn doped films are known to depend upon AsH$_3$ partial pressures. Therefore, Zn incorporation changes with temperature and decomposed AsH$_3$ concentration. Above 600 °C AsH$_3$ is fully decomposed and Zn incorporation is temperature dependent. For a given TMGa, DMZn, and AsH$_3$ mole fraction the hole concentration and Hall mobility is also seen in Fig. 2. The hole mobility exhibited a decrease with decreasing growth temperature. This phenomena can be interpreted in terms of pronounced Zn evaporation from the surface of epilayers at higher growth temperature. Another mechanism that may explain these results is temperature dependence of gallium vacancies. Chang *et al.*[27] and Glew[34] observed similar behavior of Zn doped GaAs by low pressure MOVPE reactor using diethylzinc (DMZn) and both DMZn and DEZn, respectively.

2. Effect of AsH$_3$ mole fraction

The hole concentration and growth rate versus AsH$_3$ mole fraction is illustrated in Fig. 3, for a given TMGa and DMZn mole fraction. The hole concentration showed a near linear variation with increasing AsH$_3$ flow rates, which is in agreement with the earlier reported results by Bass and Oliver,[35] while the growth rates were affected with a linear decrease. A vacancy-controlled model may be considered to explain such behavior. In the TMGa–AsH$_3$ system, the leading reaction to the formation of GaAs can be expressed as:

$$(CH_3)_3Ga+3/2H_2+V_{Ga}\overset{K_1}{\rightleftarrows}Ga_{Ga}+3CH_4, \qquad (1)$$

$$AsH_3+V_{As}\overset{K_2}{\rightleftarrows}As_{As}+3/2H_2, \qquad (2)$$

where K_1 and K_2 are the equilibrium constants of the above reactions, then

$$\frac{[V_{Ga}]}{[V_{As}]}=\frac{K_2}{K_1}\,\frac{P^3_{CH_4}P_{AsH_3}}{P_{TMGa}P^3_{H_2}}. \qquad (3)$$

An increase in P_{AsH_3}/P_{TMGa} will increase in gallium vacancy concentration, hence, the incorporation of Zn on the Ga site is increased. The hole concentration is thus increased when the AsH$_3$ mole fraction is increased.

According to analysis of Vechten,[36,37] the vacancy migration reaction occurring in GaAs growth is expressed as:

$$As_{As}+V_{Ga}\rightleftarrows As_{Ga}+V_{As}. \qquad (4)$$

Here As must obtain enough energy to overcome the energy barrier. When the growth temperature decreases, the above reaction occurs towards the left and more gallium vacancies tend to appear. Since the incorporation of Zn is proportional to Ga vacancy, the Zn concentration on Ga sites increases under the lower growth temperatures.

3. Effect of growth temperature on growth rate

The growth rate is a function of growth temperature for Zn doped GaAs as shown in Fig. 4. It can be seen from the figure that the growth rate increases with increasing growth temperature up to 625 °C. But different authors observe[34] the different behavior of growth rate in the temperature range 550–750 °C. At high substrate temperatures, the growth rate decreases because of arsenic desorption effects from the growth surface. Between the temperatures 625 °C and 725 °C the growth rate was found to be temperature independent which is similar to that described by Glew.[34] In this temperature region, TMGa is fully decomposed and hence

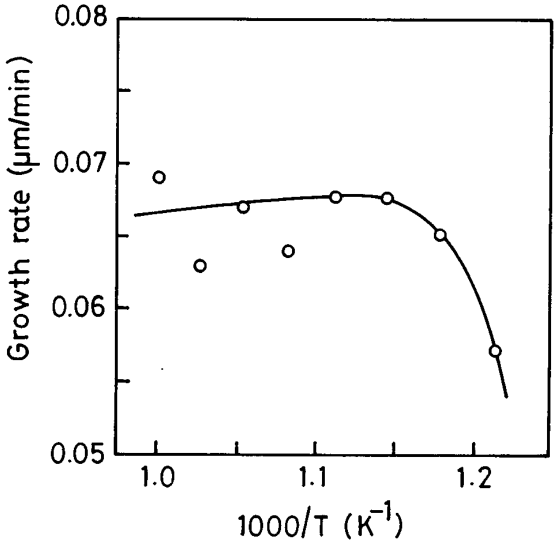

FIG. 4. Growth rate vs reciprocal of growth temperature.

growth rate becomes independent of temperature. In a classic paper, Shaw[38] showed that an examination of growth rate versus temperature allows a general categorization of the process, limiting the growth rate as either mass transport, surface kinetics, or thermodynamics. For an exothermic process such as MOVPE, increasing temperature results in a decrease in the thermodynamically limited growth rate. If the reaction rates limit the growth rate, termed the kinetically limited case, the growth rate increases with increasing temperature. Since diffusion is a nearly temperature independent process, the growth rate is nearly independent of substrate temperature in the mass-transport-limited case. The growth rate is nearly independent of temperature of MOVPE growth process in the temperature range from 550 °C to 750 °C, at normal operating pressure. This is indicative of mass-transport-limited growth. At lower temperature, the growth rate decreases with decreasing temperature, characteristic of a process limited by reaction kinetics. The growth rate is proportional to the flux of atoms being transported, usually by diffusion, through the gas phase to the interface, which is identical to the flux of atoms crossing the interface into the solid. Using ordinary growth conditions, keeping temperature between approximately 550 °C and 800 °C, this is the normal situation for MOVPE growth of GaAs, the growth rate is nearly independent of temperature in the mass-transport-limited growth. For surface kinetically limited process, the growth rate increases exponentially with increasing temperature. This occurs for the MOVPE growth of GaAs only at temperature below approximately 550 °C. Since the MOVPE growth process is in the mass-transport-limited regime, the growth rate is linearly dependent on the group III partial pressures not the group V partial pressure, which controls the stoichiometry of the semiconductor. This is important because the stoichiometry affects the dopant and impurity incorporation as well as the concentrations of native defects, i.e., those involving interstitial atoms and vacancies.

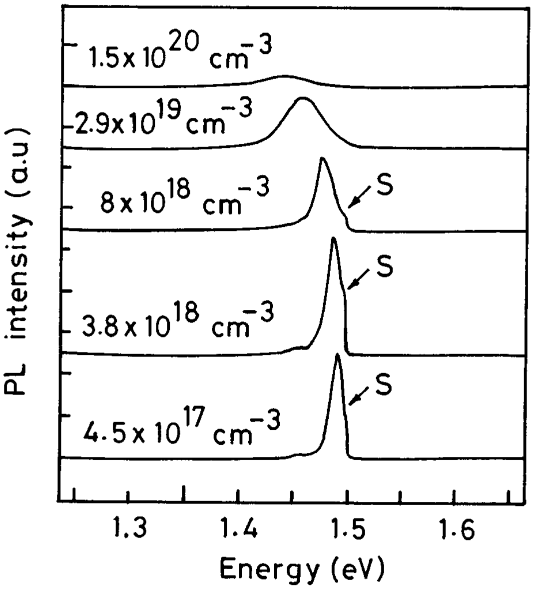

FIG. 5. 4.2 K PL spectra of Zn doped GaAs epilayers for various hole concentrations.

It is observed that the higher the substrate temperature (T_{sub}), the higher the available gallium concentration and hence the higher the growth rates.

B. Optical properties

1. PL spectra as a function of hole concentrations

Figure 5 shows the 4.2 K PL spectra of Zn doped GaAs for hole concentrations of

(a) 4.5×10^{17} cm^{-3},
(b) 3.8×10^{18} cm^{-3},
(c) 8×10^{18} cm^{-3},
(d) 2.9×10^{19} cm^{-3}, and
(e) 1.5×10^{20} cm^{-3}, respectively.

The curves were intentionally offset along the y axis with respect to each other for better clarity. The same procedure was used for all the other PL spectra in this article. The shoulder peak labeled 'S' appeared at the doping concentrations of $p\geqslant3.8\times10^{18}$ cm^{-3}, as the arrow indicates. The 'S' peak is prominent at a hole concentration of 8×10^{18} cm^{-3} and disappears at higher hole concentrations. This peak is not to be seen at 120 K PL spectra. This 'S' peak becomes more obvious as the temperature decreased or the hole concentration increased.[25] The origin of the 'S' peak is not yet clearly understood. Szmyd and Majerfeld[31] suggested that the shoulder peak (1.38 eV) was due to the band bending between the heavily carbon doped layer and the semi-insulating substrate. The high energy shoulder peak beside the main peak has been explained as being due to the K-nonconversing process related to the Fermi level,[8] but may be found in contrast with the arguments of Sernelius.[32] Chen *et al.*[17] claimed that the low energy shoulder peak (1.38 eV) represents the (e–A) transition. But the shoulder peak at 1.485 eV for Zn doped GaAs is independent of hole concentration and this shoulder peak was due to the transition between the conduction band and the bottom of the impurity band and not the K-nonconserving process related to the Fermi level. Kim *et al.*[12] suggested that the shoulder peak for C-doped GaAs, which appears on the higher energy side, is mainly due to the conduction band and the heavy hole valence band (CB–HH) transition. Most recently Lee *et al.*[29] concluded that the shoulder peak at 1.495 eV is the luminescence of the semi-insulating (SI) substrate, and suggested that the luminescence of the substrate must be taken into account when optical properties of heavily doped epitaxial layers on the substrate are studied by using PL spectroscopy at low temperature. The FWHM, $\Delta E(p)$ of the $(e-A)$ peak at 4.2 K of PL spectra increases with increasing hole concentration. The broadening of FWHM is similar to the C doped GaAs,[12] Be doped GaAs,[18] and Zn doped GaAs[8] and can be explained by band-to-band optical transitions with and without momentum (K) conservation between the conduction and valence bands.[8] Alternatively, this can be explained as the impurity band merges with the valence band edge and it becomes band tail states at high doping concentrations. Because of this phenomena, the optical transitions between the conduction and valence band are broadened, and the FWHM of PL spectra increases. The $\Delta E(p)$ increases slowly up to $p \cong 1\times10^{18}\ \mathrm{cm}^{-3}$ and increases rapidly with increasing hole concentration. From the data we have obtained an empirical relation for FWHM of Zn doped GaAs,

$$\Delta E(p)(\mathrm{eV}) = 1.15\times10^{-8} p^{1/3} \tag{5}$$

with the concentration range between 1×10^{17} and $1.5\times10^{20}\ \mathrm{cm}^{-3}$. The results are compared with C doped GaAs[17] and shown in Fig. 6. The value of FWHM is about 10 meV for $p=1\times10^{18}\ \mathrm{cm}^{-3}$, and it increases rapidly at $p>3\times10^{18}\ \mathrm{cm}^{-3}$ due to the appearance of the extra peak (labeled 'S' in Fig. 5). When the concentration reaches $1.5\times10^{20}\ \mathrm{cm}^{-3}$, the value of FWHM is 50 meV. The shoulder peak is independent of hole concentration and disappears at concentration greater than $8\times10^{18}\ \mathrm{cm}^{-3}$. The shoulder peak on the high energy side of the main peak has often been observed in the PL spectra of highly doped GaAs samples.

2. Band gap shrinkage due to doping effect

The main peak energy shifted to lower energy as the hole concentration increased, which is primarily because of doping induced band gap shrinkage or band gap narrowing (BGN). Figure 7 shows the main PL energy with the hole concentrations in the range of 1×10^{17}–$1.5\times10^{20}\ \mathrm{cm}^{-3}$. For multilayer structures, the PL peak position, E_p, is much easier to confirm even when the emission from other layers are present.[28] Therefore, the E_p-p relation is very important for the determination of hole density in the base of HBTs. The empirical relation for E_p-p can be represented by

$$E_p = 1.52 - 4.1\times10^{-6}\, p^{0.215}. \tag{6}$$

We have included the results presented by other workers in the open literature for comparison.[8,14–18,25,29] It is very difficult to extract the exact band gap shift from the PL spectra because of lifetime broadening effects.[32] We determined the band gap, E_g, of heavily doped GaAs, by a linear extrapolation to the energy axis, using a function of the type $f(E) = A(E-E_g)^{1/2}$, of the spectrum to the background level following the work by Olego and Cardona.[8] This method was used by several authors for determination of E_g.

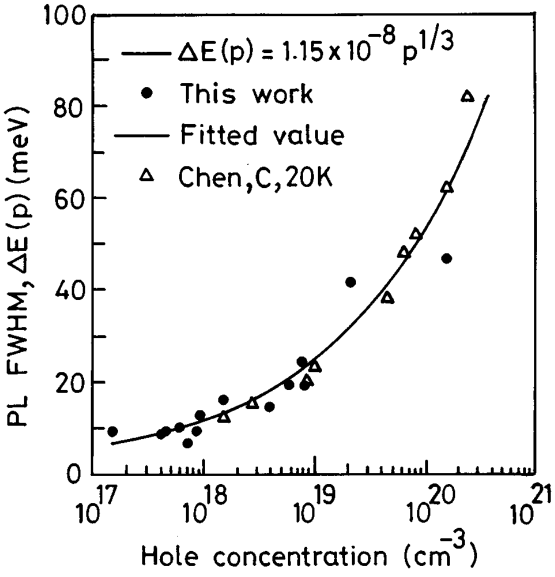

FIG. 6. FWHM of 4.2 K PL vs hole concentrations.

Figure 8 shows the band gap shrinkage of Zn-doped GaAs in the range 4.5×10^{17}–$1.5\times10^{20}\ \mathrm{cm}^{-3}$, as a function of hole concentration. In this figure, we have also plotted the reported results for Zn, Be, and C doped GaAs measured at temperatures between 4.2 and 77 K, as the band gap shrinkage is independent of temperature.[8] The measured band gap shrinkage of carrier concentration of Be, C, and Zn doped GaAs, exhibited consistent agreement among each other.[8,10,12,18,19,25,29] In general, the band gap shrinkage is proportional to the hole concentration of the form $p^{1/3}$, thus it can be represented by

$$\Delta E_g = E_g(\mathrm{doped}) - E_g(\mathrm{pure}) = -Bp^{1/3}, \tag{7}$$

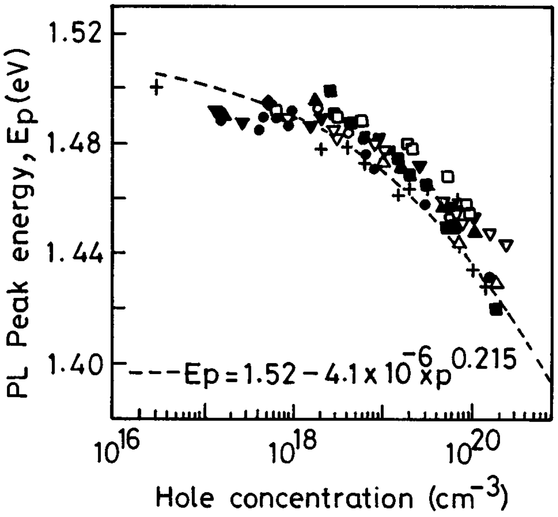

FIG. 7. 4.2 K PL peak energy E_p as a function of hole concentration: (----) fitted value, (●) this work, (▲) Ref. 8, (▼) Ref. 14, (♦) Ref. 18, (+) Ref. 15, (■) Ref. 29, (○) Ref. 16, (▽) Ref. 25, (△) Ref. 25, (□) Ref. 17.

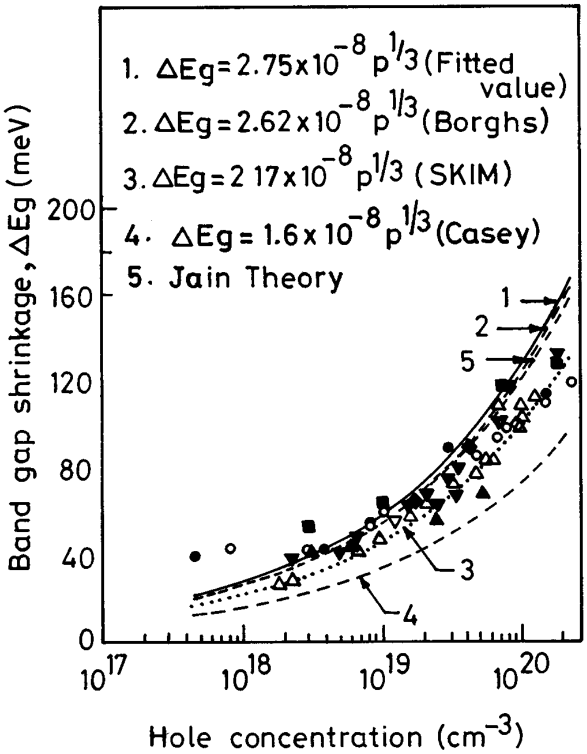

FIG. 8. The band gap shrinkage of Zn doped GaAs epilayers as a function of hole concentration: (●) this work, (▼) Ref. 29, (△) Ref. 19, (▲) Ref. 10, (♦) Ref. 8, (■) Ref. 25, (○) Ref. 25.

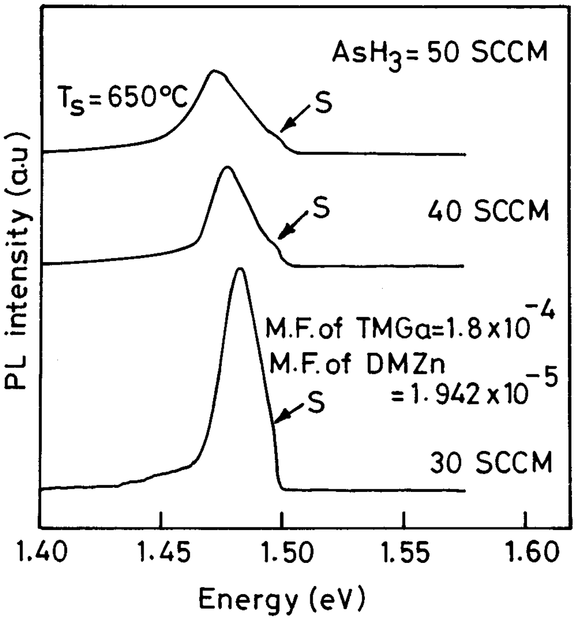

FIG. 9. 4.2 K PL spectra of Zn doped GaAs epilayers as a function of AsH_3 flow rate.

where B has been adjusted to give the measured value of E_g at higher hole concentrations and the minus sign signifies the band gap shrinkage at higher concentrations. The empirical relation for band gap narrowing with our data can be written as

$$\Delta E_g = -2.75\times 10^{-8} p^{1/3}, \tag{8}$$

where E_g is in eV and p in cm^{-3}. We have made an attempt to fit our experimental data to the expression suggested by Jain,[39]

$$E_g = E_g(0) - \Delta E_g(p), \tag{9}$$

where $\Delta E_g(p) = a\times p^{1/3} + b\times p^{1/4} + c\times p^{1/2}$, a, b, and c are the coefficients that represent the effects of the BGN due to majority-majority carrier exchange, minority-majority correlation, and carrier–ion interaction respectively. For p-type GaAs, the constants a, b, and c are 9.83×10^{-9}, 3.9×10^{-7}, and 3.9×10^{-12}, respectively, where p is the hole concentration in cm^{-3} and $E_g(p)$ in eV. The band gap shrinkage result also plotted in Fig. 8 is given by Casey and Stern.[40] These relations are considered to provide a useful tool for determination of hole concentration in Zn doped GaAs by low temperature PL measurement.

3. Effect of AsH_3 variation on PL spectra

To observe the effect of the V/III ratio on the optical properties of Zn doped GaAs, the PL measurement were carried out at 4.2 K specifically on those samples grown at different AsH_3 flow rates. Figure 9 shows the PL spectra of Zn doped GaAs for fixed TMGa, DMZn mole fractions. The three curves represent three different AsH_3 flow rates. It is seen from the figure that the PL main peak energy shifted to lower photon energies and the shoulder peak appeared at the higher energy side. Since the hole concentration depends on the Ga vacancy and hence AsH_3 partial pressure [from Eq. (3)], the peak shifts due to the band gap narrowing effect. We are reporting for the first time to our knowledge, the luminescence properties of Zn doped GaAs with the AsH_3 mole fraction variation. The hole concentration increases with the increasing V/III ratio for a given TMGa mole fraction and growth temperature of Zn doped GaAs, which is the same as described by Chang *et al.*[27] This can be explained by the vacancy controlled model as described in Eq. (3). But completely different observation had been made by Hanna *et al.*,[11] that for a given growth temperature the hole density p decreases with increasing V/III ratio for C doped GaAs using CCl_4 as a source of carbon.

4. Effect of PL measurement temperature

The PL emission spectra at various temperatures were investigated and shown in Fig. 10. The PL line shapes became sharper and shifted to higher energy as the temperature decreased. Figure 10 shows the PL spectra measured at 300, 120, and 4.2 K for Zn doped GaAs with $p = 8\times 10^{18}\ \mathrm{cm}^{-3}$. A minute shoulder peak at the high energy side of the main peak was observed; this peak is more obvious as the temperature decreased or the concentration increased. The main peak is shifted to the high energy side as the temperature is decreased. Olego and Cardona[8] have shown that the Varshni equation is valid for heavily doped materials, assuming $E_g(0)$ represents the actual band gap of the material at 0 K, α and β are adjustable parameters. This equation can be expressed as

$$E_g(T) = E_g(0) - \alpha T^2/(\beta + T), \tag{10}$$

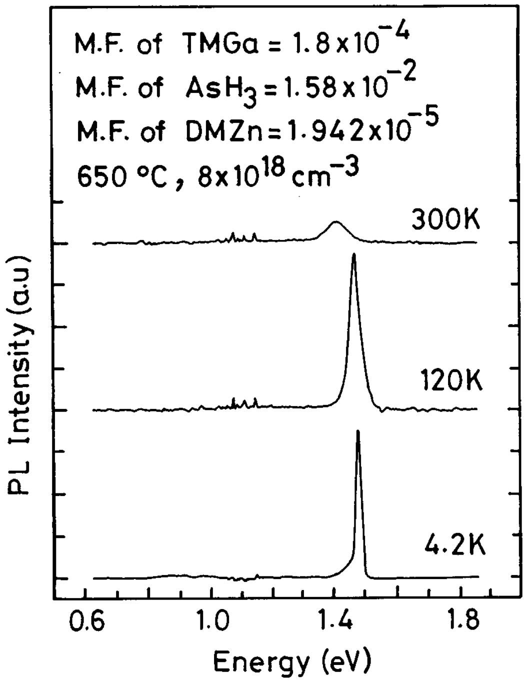

FIG. 10. PL spectra of Zn doped GaAs at 300, 120, and 4.2 K indicating the appearance of a shoulder peak.

which describes the main peak variation for different temperatures for most of the semiconductors. The peak energy shift at various temperatures for C and Zn doped GaAs are described by Chen *et al.*[17] and Kim *et al.*[12] The function $E_g(T)$ is provided by a set of PL spectra collected at different temperatures, as in Fig. 10. The temperature dependence of $E_g(T)$ is mainly a consequence of carrier–phonon interactions. At 300 K, the band gap energy is modified by intervalence–band phonon interactions, which are enhanced for hole states extending deeply into the bands as the energy dispersion relations for the light and heavy holes becomes essentially parallel. The band gap of GaAs is much more sensitive to carrier–phonon interactions than Si. This may explain the noticeable effect of temperature on the E_g-p relation for GaAs. At low temperatures, carrier–phonon interactions are greatly reduced, and hence the band gap is increased at a specific hole concentration.

IV. CONCLUSION

Zn doped GaAs epitaxial layers grown by low pressure metalorganic vapor phase epitaxy in the hole concentration range 1×10^{17}–1.5×10^{20} cm^{-3} have been investigated by photoluminescence as a function of hole concentrations and temperature. From the PL spectra we have obtained an empirical relation of FWHM and band gap shrinkage as a function of hole concentrations. These relations are considered to provide a useful tool for determining the hole concentration by low temperature PL measurement. The $(e-A)$ peak shifts to the low energy side as the hole concentration increases. The $(e-A)$ peak also shifts to the low energy side as the AsH$_3$ mole fraction increases. This has been explained by the vacancy controlled model.

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